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(54) Title: SOLDER ALLOY

(57) Abstract: A lead-free solder alloy suitable for use in wave soldering and, in particular with water base VOC-free flux, low-VOC (water base) flux and low solids (solvent base flux consists of tin to which is/are added one or more of Ag in an amount of up to 10 %, Cu in an amount of up to 5 %, Sb in an amount of up to 10 % and Bi in an amount of up to 10 %, which alloy additionally contains phosphorus in an amount of up to 0.01 %, all percentages being on weight basis related to the amount of tin.

SOLDER ALLOY

This invention relates to solder alloys and in particular solder alloys for use in soldering methods that use a reservoir of molten solder.

The most commonly used solder materials have hitherto been tin-lead solders. Apart from the problem of using lead-containing alloys which are environmentally unfriendly, in particular tin-lead alloys, the molten solder oxidises and thereby prevents the surface from looking bright and clear. Phosphorus has, indeed, become a widely used additive to tin-lead solders in amounts of 0.001 - 0.004 per cent. Such addition slows down the rate at which the molten solder oxidises and prevents the formation of coloured interference films of oxide and keeps the surface looking bright and clear. A further advantageous effect is to break up the "wet" dross containing a high proportion of unoxidised solder formed on wave soldering machine solder pots into a more powdery, drier dross with less unoxidised metal. Apart from reducing the amount of oxide and dross formed, phosphorus addition confers no particular advantage in terms of reduced incidence of soldering defects.

Wave soldering with the now preferred lead-free alloys such as SnAg3.8Cu0.7 and SnCu0.7, especially when working with low solids (solvent base) fluxes, has led to the identification of a tendency for a tenacious oxide layer to form on the wave which can cause soldering defects such as webbing and bridging. Overall, there is an increase in defect rates if such oxide layer is able to form. Such problem may also occur with other soldering methods that use a reservoir of molten solder, including drag soldering and methods using a small solder fountain or wave.

According to one aspect of the present invention,

there is provided a lead free soldering alloy which consists of tin to which is/are added one or more of Ag in an amount of up to 10 per cent, Cu in an amount of up to 5 per cent, Sb in an amount of up to 10 per cent and Bi in an amount of up to 10 per cent, which alloy additionally contains phosphorus in an amount of up to 0.01 per cent, all percentages being on a weight basis related to the amount of tin.

The phosphorus addition can be carried out at the stage of manufacture of the lead free alloy or by addition of concentrate pellets of solder alloys with phosphorus to the solder pot for use in the soldering method.

It has been found that by having, in particular from 0.001 - 0.004 per cent phosphorus present in a wave soldering bath or other source of lead free alloy as defined above, oxide is substantially eliminated from the wave. Moreover, when using lead-free alloys such as SnAg3.5-4 Cu0.5-1 and SnCu0.5-1, especially SnAg3.8Cu0.7, in particular, defect rates obtained are similar to those achieved with a tin-lead solder. The oxide layer on the wave becomes much less tenacious. Rosin base fluxes with solids contents of 10% by wt. and above may not need the benefit of this invention, P can be omitted as the rosin can cope with the oxide and keep the wave clear.

In a second aspect, this invention provides a method of attaching a circuit component to a substrate, which comprises carrying out soldering using a soldering alloy according to the first aspect of the invention.

Use of phosphorus containing lead free alloys in soldering methods that use a reservoir of molten solder, in particular in wave soldering technology, but also in, for example, drag soldering and methods using a small solder fountain or wave, has a beneficial

effect on oxidation and drossing and in particular in suppressing formation of a tenacious oxide layer at the most critical parts of the molten solder, in particular the wave. It also leads with lead free solders and water base VOC-free or low VOC water base, as well as low solids solvent base fluxes to soldered printed circuit boards showing significantly lower defects than when phosphorus has not been added.

CLAIMS

1. A lead free soldering alloy which consists of tin to which is/are added one or more of Ag in an amount of up to 10%, Cu in an amount of up to 5%, Sb in an amount of up to 10% and Bi in an amount of up to 10%, which alloy additionally contains phosphorus in an amount of up to 0.01%, all percentages being on weight basis related to the amount of tin.

2. An alloy according to claim 1, which contains from 0.001 to 0.004% of phosphorus.

3. An alloy according to claim 1 or 2, wherein the phosphorus is present in SnAg3.5-4.0 Cu0.5-1.

4. An alloy according to Claim 3, wherein the phosphorus or SnCu0.5-1 is present in SnAg3.8Cu0.7.

5. A method of attaching a circuit component to a substrate, which comprises carrying out soldering using a soldering alloy according to any preceding claim in forming a joint between circuit component and a conductive element on the substrate.

6. A method according to claim 5, which is a wave soldering method.

7. A method according to claim 5, which is a drag soldering method or a method using a solder fountain.

8. A method according to claim 5, 6 or 7 wherein soldering is carried out with water base VOC-free flux, low-VOC (water base) flux and low solids (solvent base) flux.

9. A method according to claim 8, wherein soldering is carried out with rosin base flux having a solids content of less than 10% by wt.

10. A solder joint whenever produced using a soldering alloy according to any one of claims 1 to 4 or a method according to any one of claims 5 to 9.

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A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 13, 30 November 1998 (1998-11-30) & JP 10 225790 A (SAMSUNG), 25 August 1998 (1998-08-25) abstract	1,2
P,X	& US 5 980 822 A (SAMSUNG) 9 November 1999 (1999-11-09) claim	1,2
X	EP 0 336 575 A (COOKSON GROUP PLC) 11 October 1989 (1989-10-11) example 2	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 06, 30 April 1998 (1998-04-30) & JP 10 034376 A (NIPPON GENMA:KK), 10 February 1998 (1998-02-10) abstract	1,2
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 261 (M-514), 5 September 1986 (1986-09-05) & JP 61 086091 A (FURUKAWA ELECTRIC CO LTD:THE), 1 May 1986 (1986-05-01) abstract	1
A	DE 37 30 764 C (DEMETRON) 14 July 1988 (1988-07-14)	
A	DE 198 16 671 A (FUJI ELECTRIC CO LTD) 22 October 1998 (1998-10-22)	

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. ional Application No
PCT/GB 00/02502

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10225790 A	25-08-1998	CN 1195592 A	14-10-1998
		JP 2885773 B	26-04-1999
		US 5980822 A	09-11-1999
EP 0336575 A	11-10-1989	AU 3167289 A	05-10-1989
		CA 1299470 A	28-04-1992
		JP 2070033 A	08-03-1990
		US 4929423 A	29-05-1990
		ZA 8902041 A	28-03-1990
JP 10034376 A	10-02-1998	NONE	
JP 61086091 A	01-05-1986	NONE	
DE 3730764 C	14-07-1988	BR 8804611 A	18-04-1989
		EP 0307638 A	22-03-1989
DE 19816671 A	22-10-1998	JP 10286689 A	27-10-1998
		JP 11058066 A	02-03-1999
		JP 11077366 A	23-03-1999